

Second harmonic generation from oxazine dyes at the air – water interface

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Abstract

Several oxazine laser dyes have been studied at the air – water interface by the surface-specific technique of second harmonic generation (SHG). Bulk absorption measurements indicate the formation of aggregates in aqueous solutions of oxazine 720, cresyl violet, and nile blue. The SHG appears to originate almost exclusively from dimers previously identified as H-aggregates. Addition of salt (NaCl, NaI, and KNO₃) to the solution increases the SHG to a much greater extent than it promotes bulk aggregation, suggesting that the surface dye concentration and/or the dimer equilibrium constant at the surface increases with ionic strength. The anisotropy of the SHG signals was measured and used to comment on the orientation of the aggregate molecules at the interface.

Why study interfaces?

Interfaces are involved in many physical / biological / atmospheric systems

Examples of previous studies

- pH¹
- pK_a^{2,3}
- Surface polarity from solvent shifts⁴
- Values are often the linear average of the two bulk values

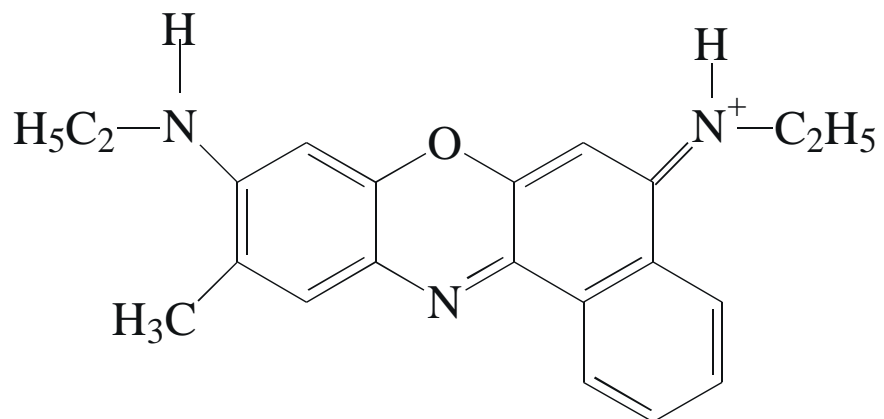
For what properties are the interface properties similar to an average of the bulk phases and when are they significantly different?

Why study dye aggregates?

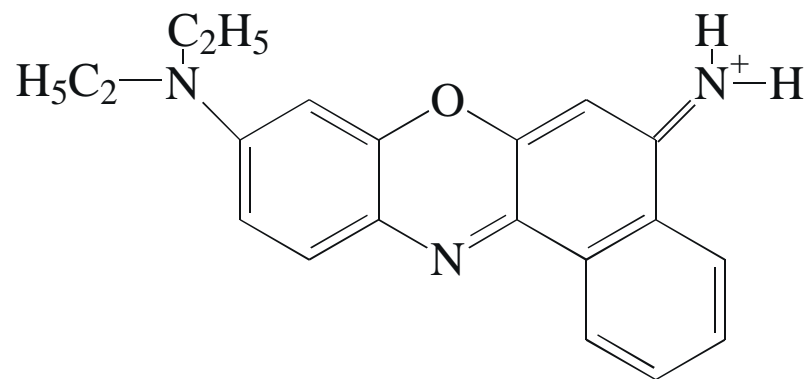
- Industrial Applications
 - Photography, photovoltaic cells
 - Laser dyes – well characterized in the bulk
- H & J aggregates
Extensive bulk studies for comparison

Structures of dyes in study

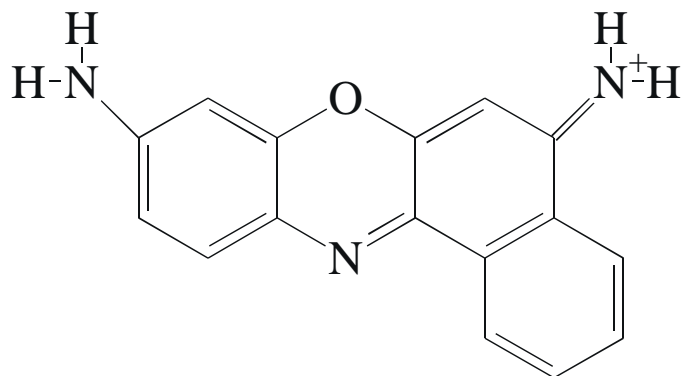
Oxazine 720



Nile Blue



Cresyl Violet



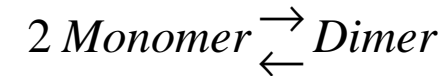
Overall approach

Compare properties of dye aggregates at the air / water interface to the aqueous bulk

Step 1: Characterize properties of interest for bulk

- Peak positions and relative intensities
- K_d for aqueous bulk solutions

For the reaction



K_d can be expressed as

$$K_d = \frac{[d]}{[m]^2}$$

- Effect of bulk solution composition (NaCl, surfactant)

Measurements for studying bulk solutions

UV / VIS linear absorption spectra as function of

- Dye concentration
- Salt (NaCl) concentration
- Surfactant (Triton X-100)

Step 2: Compare interface results to results from bulk

Second harmonic spectroscopy of interfaces

- Interface specific technique
- Few alternatives, especially for interfaces involving liquids
- Composition
 - a) Effect of bulk dye concentration
 - b) Additives used to shift K_d
 - Salt (NaCl, KI, KNO_3)
 - Surfactant (Triton X-100)
- Frequency domain studies / SHG spectra of interfacial species
 - a) Position of interface absorption bands
 - b) Changes in K_d / surface coverage
- Polarization anisotropy studies

How is orientation of surface species with respect to interface effected by the bulk phase composition?

Measurements at the air – water interface

- Composition

$I(2\omega)$ vs. [dye], [salt], [surfactant]
- Spectroscopy

$I(2\omega)$ as function of fundamental (ω)
- Polarization anisotropy

$I_p(2\omega)$ and $I_s(2\omega)$ as function of input polarization ($p = 0^\circ < \gamma < 90^\circ = s$)

H aggregates

Exciton theory of dipole - dipole coupling (Kasha⁵)

- Distance and relative orientation of monomers
- Electronic structure and spectral shift of aggregate absorption

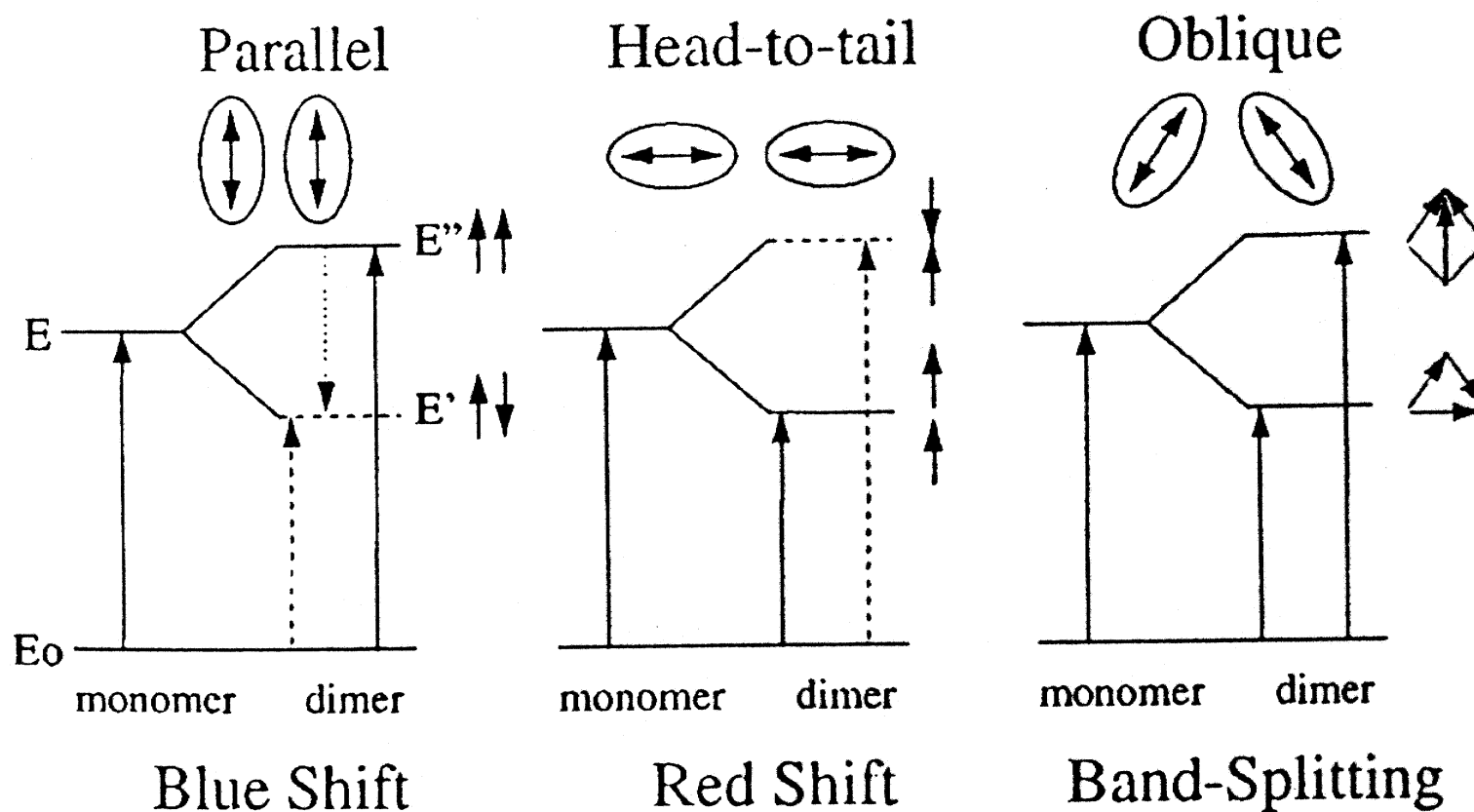


Figure taken from Reference 12, which is adapted from Reference 6. Dipole-forbidden transitions are indicated by dashed lines, dipole-allowed transitions are indicated by solid lines.

Linear Absorption Results & Discussion

Composition

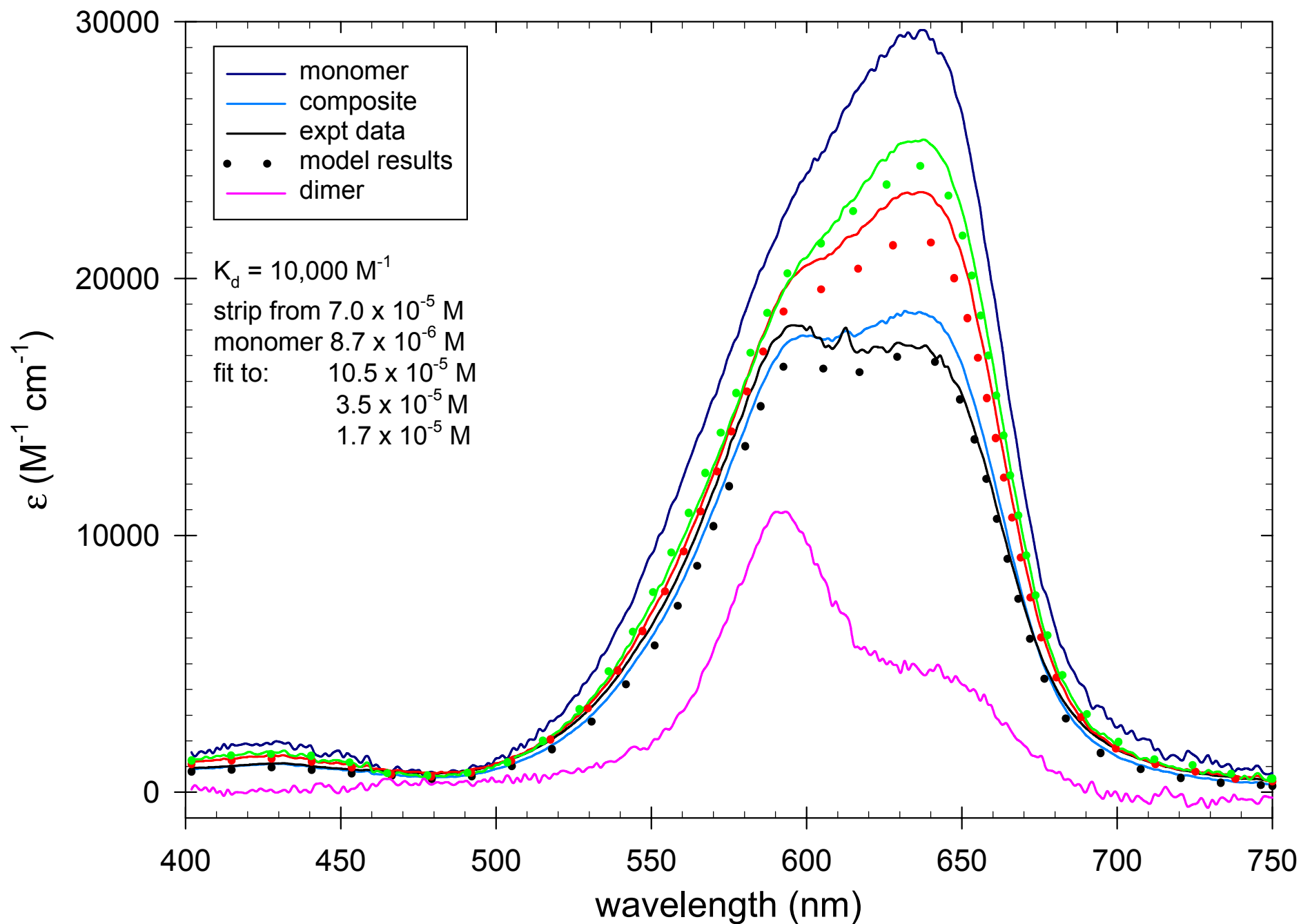
- Addition of salt (NaCl) increases K_d such that the apparent concentration is four times higher.
- Surfactant breaks apart aggregates in the bulk solution, red shifts monomer absorption ~ 10 nm.

Extracting K_d from $A(\nu)$ vs. [dye] measurements^{7,8}

Method used:

- Assume an initial value for K .
- Select monomer and composite spectra, and mathematically subtract out a dimer spectrum
- Model absorption spectra as linear combination of monomer and dimer spectra
- Refine the value of K , and repeat as necessary.

Nile Blue - Extracting K_d



K_d results

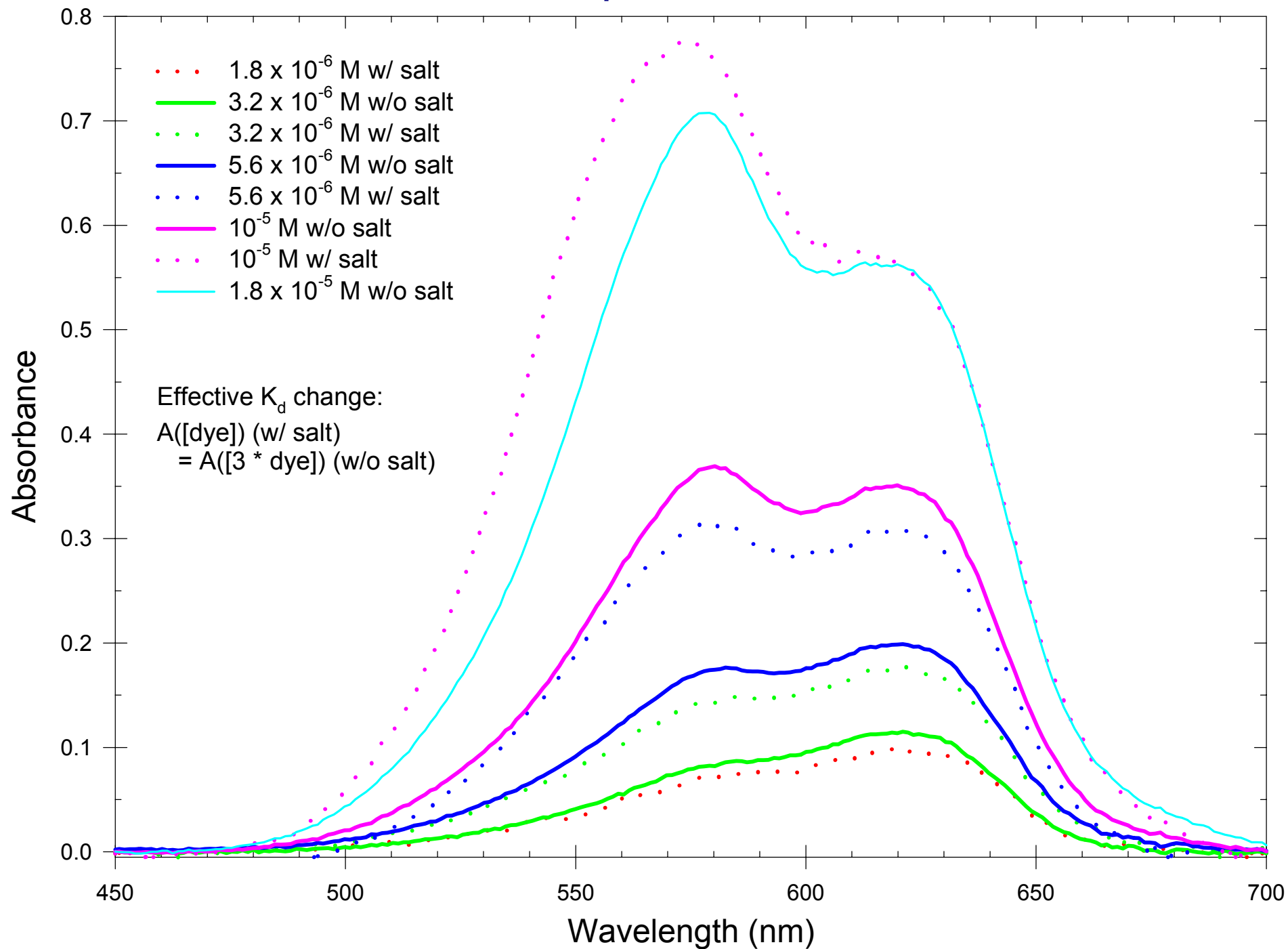
- Losses to surfaces such as cell walls make quantitative results a challenge
- relative ordering sufficient for this study

Oxazine dyes – Peak positions and relative values of K_d

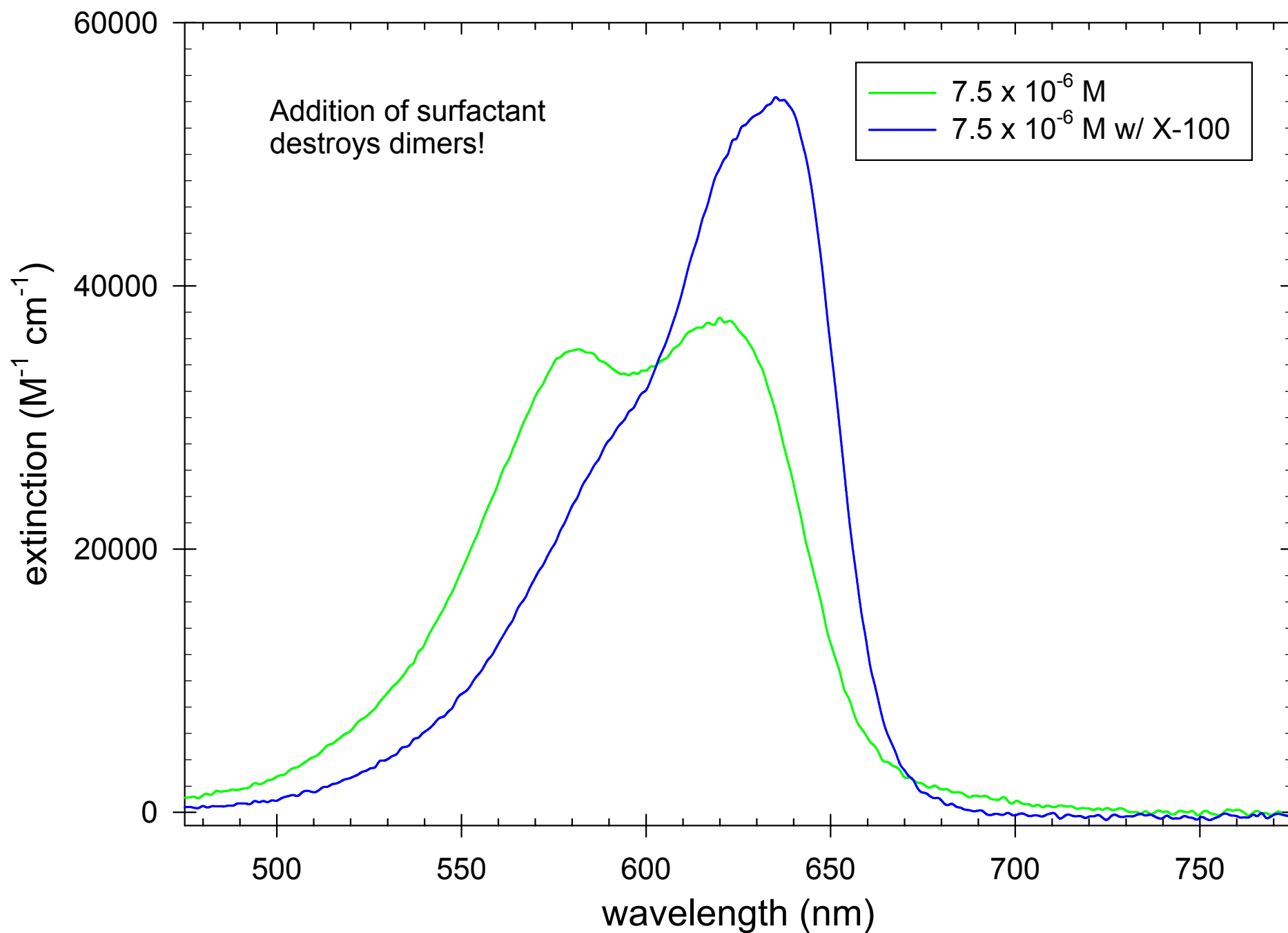
Dye	Monomer peak (nm)	Dimer peak (nm)	K_d (rel.)
Oxazine 720	620	570	37.5
		Ref. 9	$50,000 \text{ M}^{-1}$ ^a
		Ref. 10	$10^4 \rightarrow 10^5 \text{ M}^{-1}$
Cresyl Violet	580	550	2.31
Nile Blue	630	590	1

^a The reported value is $2.0 \pm 0.5 \times 10^{-5} \text{ M}$, with K_d defined as
 $K_d = m^2 / d$.

Oxazine 720 Absorption w/ and w/o 0.5 M NaCl



Oxazine 720 - Effect of Surfactant



SHG Studies of Aqueous Dye Interfaces

Dependence on composition

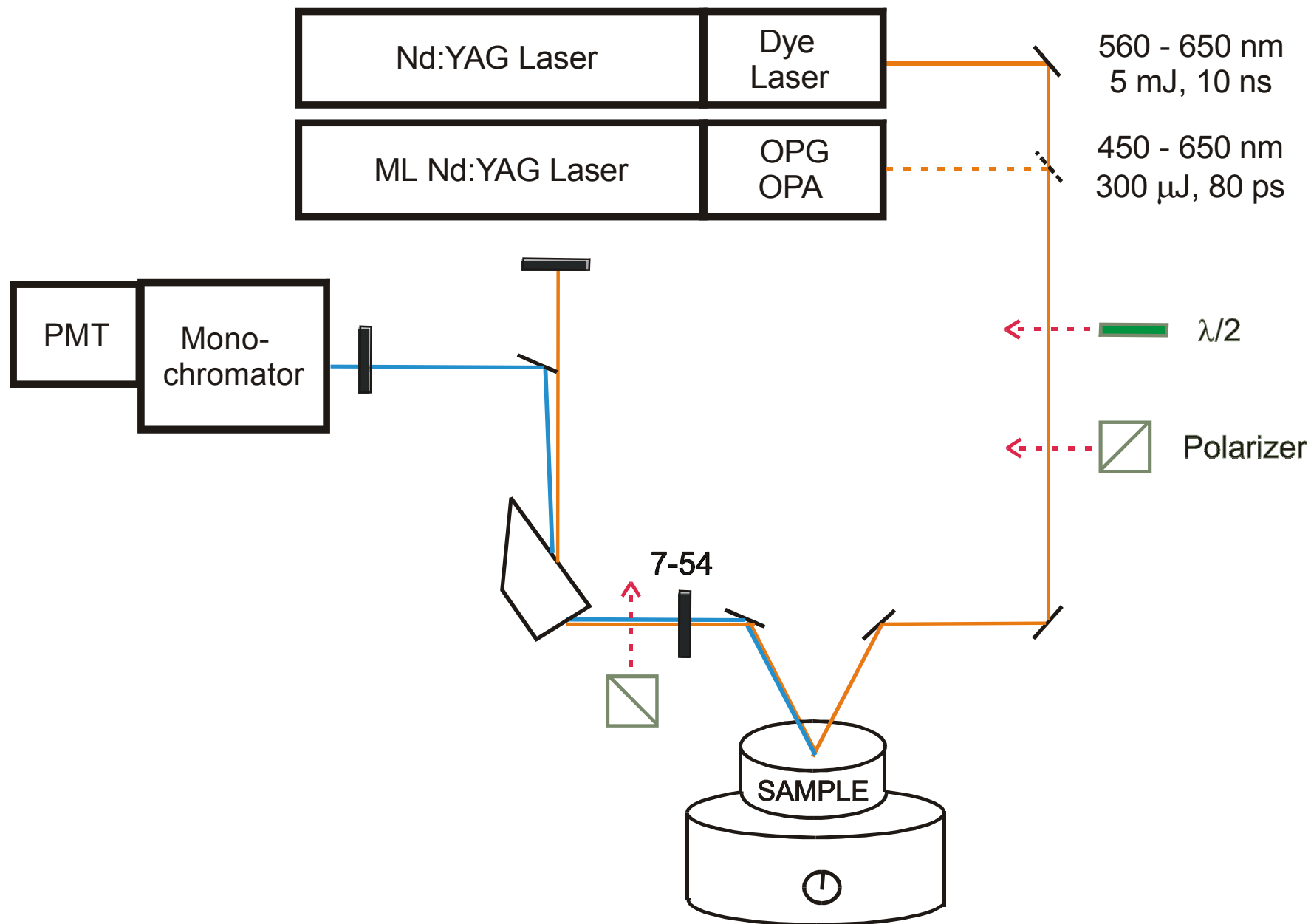
- SHG vs [dye]
 - Not unrestricted concentration dependence
 $\text{Not } I \propto D^2 \propto M^4$
 - Similar to Langmuir adsorption kinetics
$$I \propto \theta^2 \quad \theta = \frac{kM}{1 + kM}$$
 - Shift in relative absorption band intensities (dimer vs. monomer)
- [Salt]
 - Shifts monomer / dimer equilibrium at interface
 - SHG signal increases dramatically compared to K_d change
 - Consistent with *p*-nitrophenol SHG results of Das *et al*¹¹
- [Surfactant]
 - Destroys aggregates in bulk
 - Terminates SHG signal

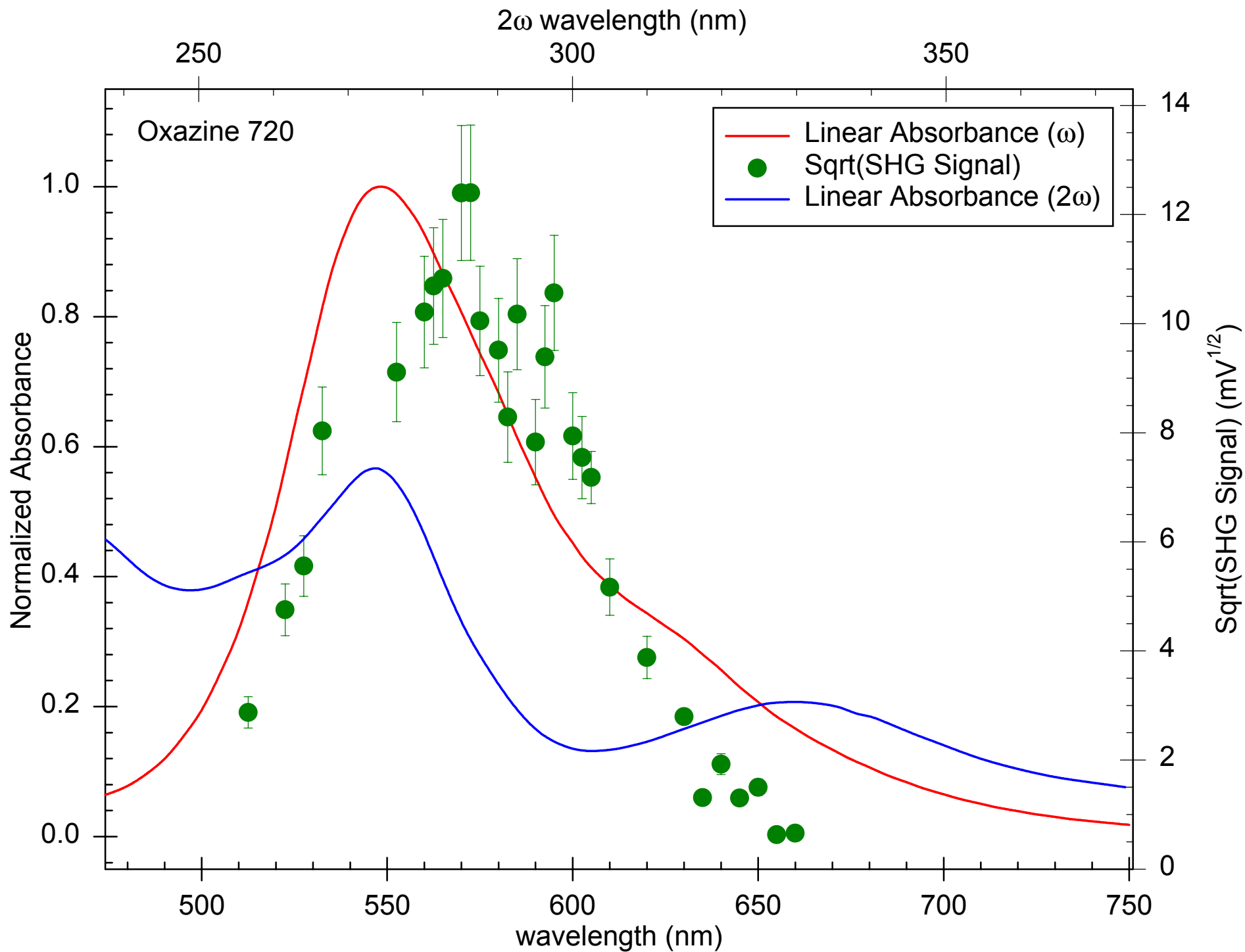
SHG is from aggregates only!

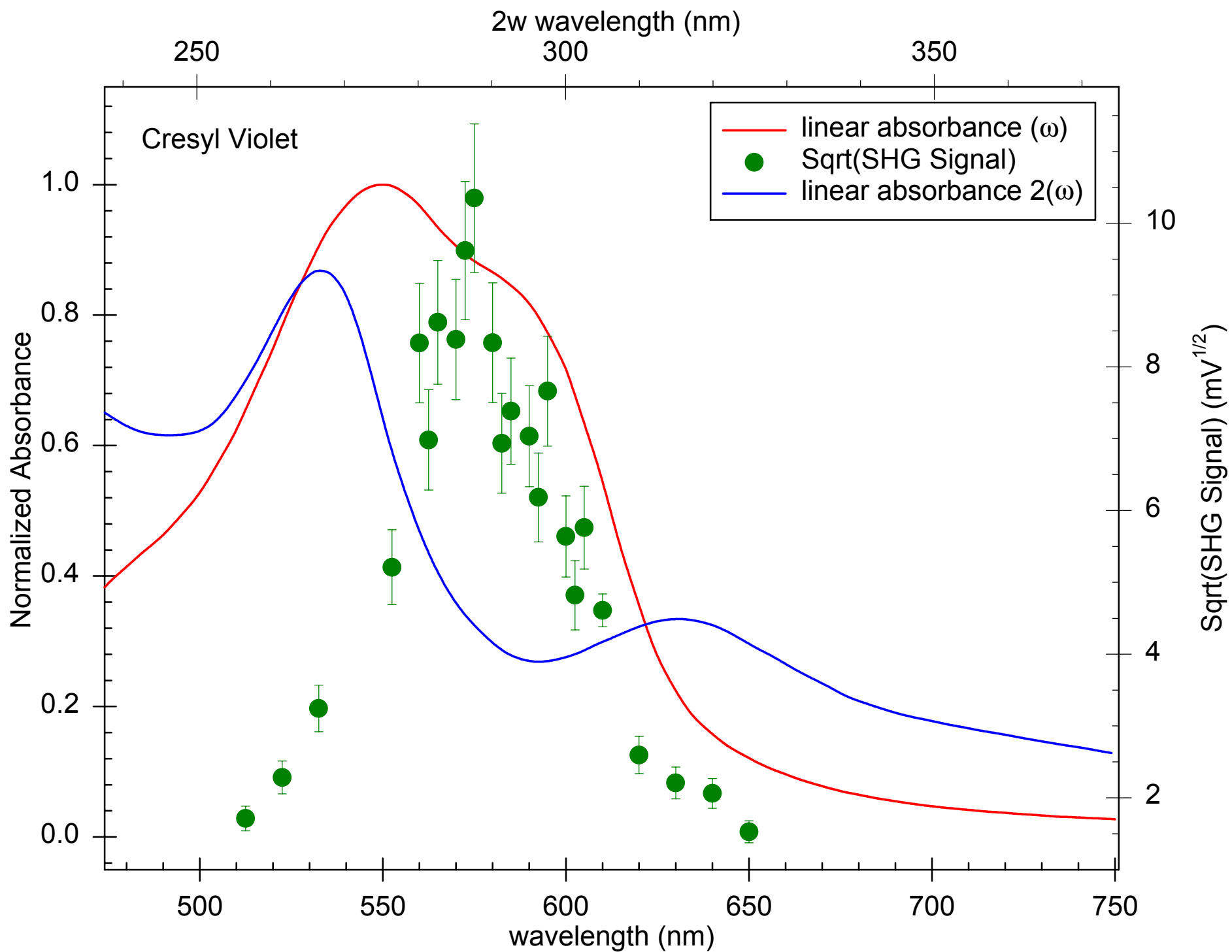
Spectra

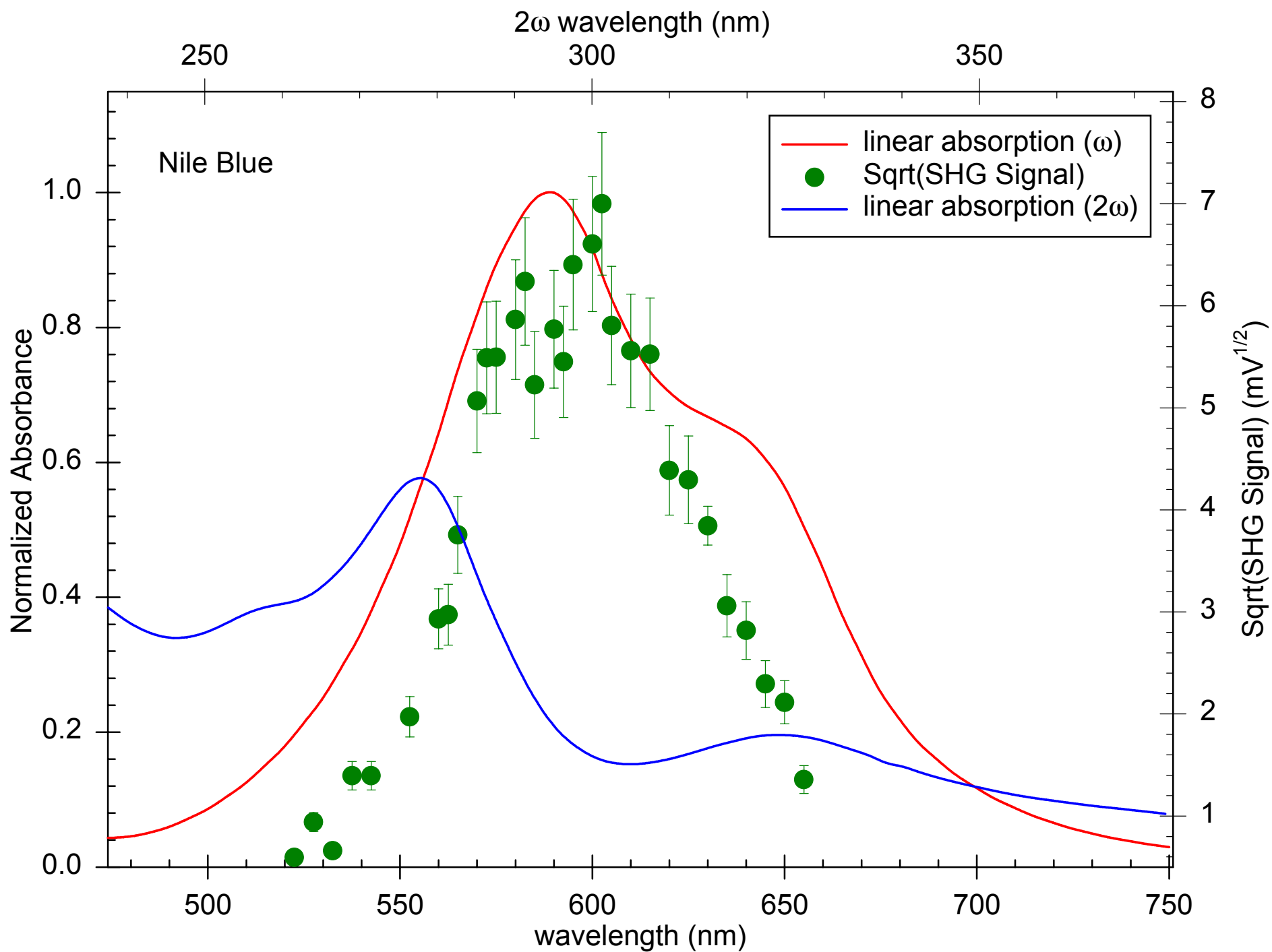
- SHG signals are narrower than bulk monomer absorption bands
- Near or slightly red shifted from dimer absorption bands
- Red shift is similar to shift observed by Leach and coworkers¹² for R6G on quartz

Detection of SHG at an Interface









SHG Polarization Dependence and Orientation

Is SHG increase with salt due to concentration or orientation?

Input (γ) and output polarization resolved I_{SHG} , $I_p(\gamma)$ and $I_s(\gamma)$:
orientational information

Methods developed and used by many groups:

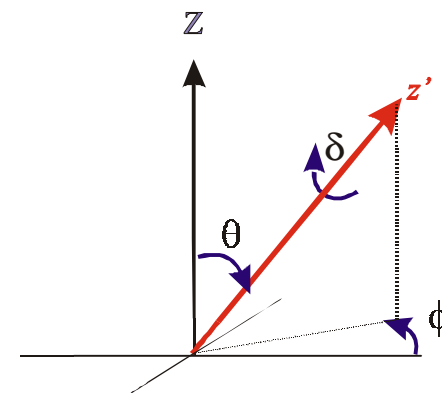
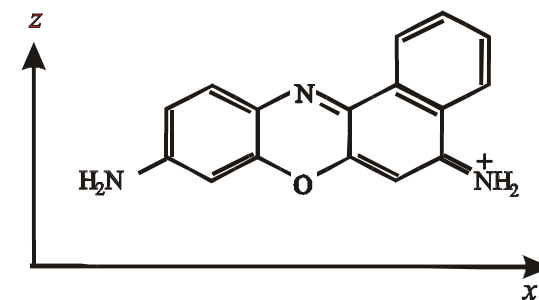
Dick¹³, Guyot-Sionnest and Shen¹⁴, Corn¹⁵

Heinz¹⁶, Girault¹⁷

Eisenthal¹⁸, Richmond¹⁹, Xu²⁰, Meech and Yoshihara²¹,

Leach^{12,22}, Frey²³

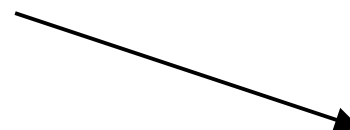
Includes: Dyes at air/solid, air/water, liquid/solid



I_s and I_p vs γ



$\chi^{(2)}_s$
susceptibilities



β 's
hyperpolarizabilities

θ, ξ
orientation of
molecular axes and
dipole

Molecular Orientation from SHG Polarization Dependence

For isotropic molecular orientation about surface normal,

3 nonzero (indep.), second order susceptibilities: $\chi_{zzz}, \chi_{zxx}, \chi_{xxz}$ ($\chi_{xzx} = \chi_{xxz}$)

SHG Polarization dependence ($\gamma = 0$ is p)

$$I_s(\gamma) = C |s_1 \sin 2\gamma \chi_{xxz}|^2 (I_\omega)^2$$
$$I_p(\gamma) = C |(s_2 \chi_{xxz} + s_3 \chi_{zxx} + s_4 \chi_{zzz}) \cos^2 \gamma + s_5 \chi_{zxx} \sin^2 \gamma|^2 (I_\omega)^2$$

$s_1 - s_5$: Coefficients for electric field at surface, linear and nonlinear Fresnel and geometric factors, including dielectric constants for bulk and interface media

χ 's (susceptibilities) related to β 's (molecular hyperpolarizabilities); orientation via $T(\phi, \theta, \delta)$

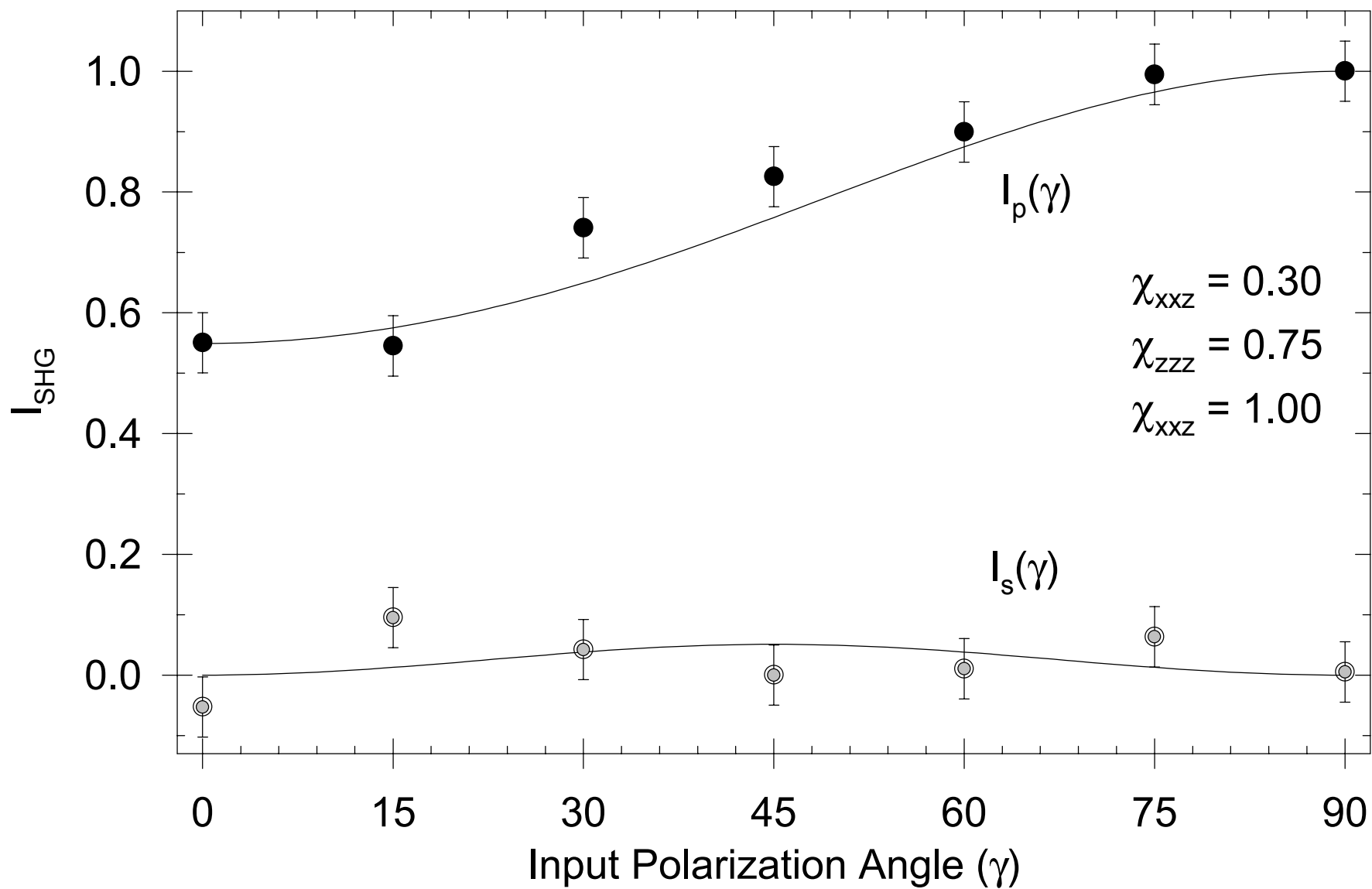
$$\chi_{IJK} = N_s \sum \langle T(\phi, \theta, \delta) \rangle \beta_{ijk}$$

Analysis (from relative χ 's) simplified by assuming:

- One or two dominant β 's
- Angle or distribution for δ (random or narrow)

SHG Polarization Dependence

Oxazine 720 - 590 nm



SHG Polarization Dependence: Results and Interpretation

NO differences within uncertainty for polarization resolved SHG for:

- Oxazine 720, Nile blue and cresyl violet, all with salt
- Nile blue with and without salt
- Several wavelengths (590 nm and 532 nm)

Increased SHG Intensity with salt NOT due to orientation effects

For Oxazine 720, $\chi_{zzz} = 0.75$, $\chi_{zxx} = 1.00$, $\chi_{xxz} = 0.3$

- More than one β_{ijk} dominant
 - If only β_{zzz} , then $\chi_{zxx} = \chi_{xxz}$
 - If only β_{zxx} , then $\chi_{zzz} = -2\chi_{xxz}$ (or with zxx and xxz transposed)
- Assume β_{zxx} and β_{xxz} dominant:
 - Analogous to other planar aromatic dyes (e.g., Rhodamines)
 - Same transition moment directions assumed for sandwich-type dimers (H-aggregates) as monomer

Orientation of Oxazine Dimers at Air-Water Interface

Derive orientation from χ 's using $T(\phi, \theta, \delta)$

- Orientation parameter: $D(\theta) = \langle \cos^3 \theta \rangle / \langle \cos \theta \rangle$
- $D(\theta)$ also in terms of χ 's; depends on dom. β '(s) and assumed δ dist.
- Heinz: explicit expression for T^{16} ; Dick: $D(\theta)[\chi]$ for most cases¹³

For β_{zxx} and β_{xxz} dominant (based on Heinz, similar to Dick for $D(\chi$'s))

$$D(\theta) = \frac{Y \chi_{zzz} + 4 \chi_{zxx} + 2\chi_{xxz}}{3 \chi_{zzz} + 4 \chi_{zxx} + 2\chi_{xxz}} \quad \text{where } Y = 3 - \langle \cos^2 \delta \rangle^{-1} \quad \text{Random: } \langle \cos^2 \delta \rangle = 1/2$$

δ	0	30	45 (random)	60
$D(\theta)$	0.86	0.82	0.72	0.45
$\theta(^{\circ})$	21.8	25.4	31.6	47.9

Following Corn¹⁵, based on Peterson and Harris²⁴,

$$\beta_r = \beta_{xxz} / \beta_{zxx} = (\chi_{zzz} + 2 \chi_{xxz}) / (\chi_{zzz} + 2 \chi_{zxx}) = 0.49 \quad - \text{ both significant}$$

Angle of x axis, ξ $\cos^2(\xi) = (1 + 2 \beta_r)^{-1} (\chi_{zzz} / (\chi_{zzz} + 2 \chi_{zxx}))$

$\xi = 68.2^{\circ}$

Conclusions

- Qualitative ordering of K_d for the dyes are reported.

Oxazine 720 >> Cresyl Violet > Nile Blue

- SHG can be used to study dimer / aggregate species at interfaces
- Salting out enhances aggregation at interface much more than in bulk solution

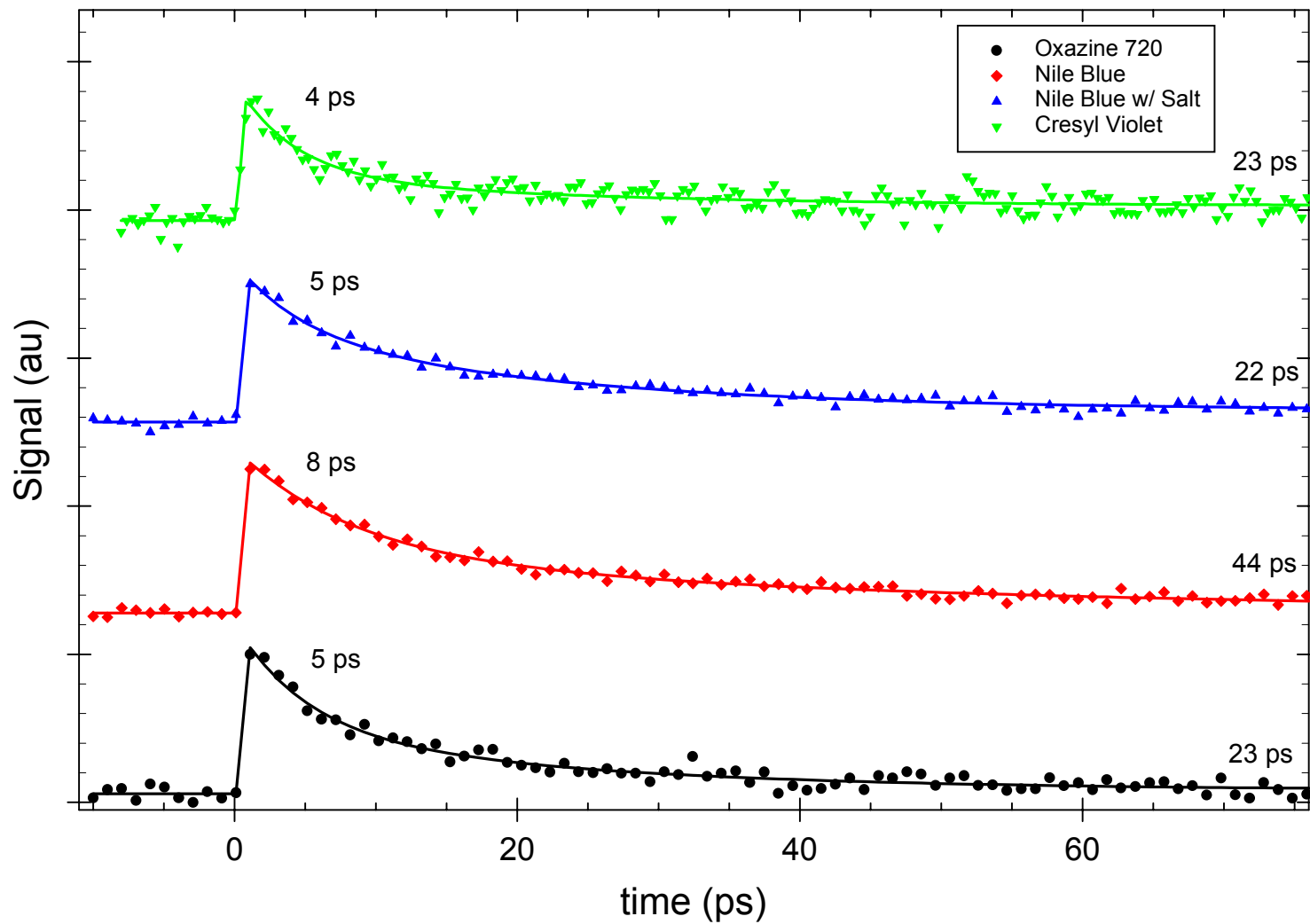
K_d (IF) >> K_d (bulk)

- The aggregates of the oxazine dyes form as H-type aggregates with similar orientation with respect to the surface normal at the interface

Future Directions

Use SHG to monitor interfacial dynamics of these dyes / aggregates

TSHG of Oxazine Dyes - 570 nm pump / probe



Acknowledgements

This work was supported by the Office of Naval Research.

This work was performed while DAS held a National Research Council - Naval Research Laboratory Research Associateship Program.

Thanks to Brad Williams and Jim Fleming (NRL) for the use of the OPG / OPA system.

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